

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 838 446 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.04.1998 Bulletin 1998/18

(51) Int. Cl.⁶: C04B 35/495, H01P 7/10

(21) Application number: 97118539.2

(22) Date of filing: 24.10.1997

(84) Designated Contracting States:

AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

(30) Priority: 25.10.1996 JP 301202/96
01.07.1997 JP 191868/97
09.10.1997 JP 293460/97

(71) Applicant:

NGK SPARK PLUG CO., LTD
Mizuho-ku Nagoya-shi Aichi (JP)

(72) Inventors:

- Yokoi, Hitoshi
Mizuho-ku, Nagoya-shi, Aichi (JP)
- Tosa, Akifumi
Mizuho-ku, Nagoya-shi, Aichi (JP)
- Ohbayashi, Kazushige
Mizuho-ku, Nagoya-shi, Aichi (JP)

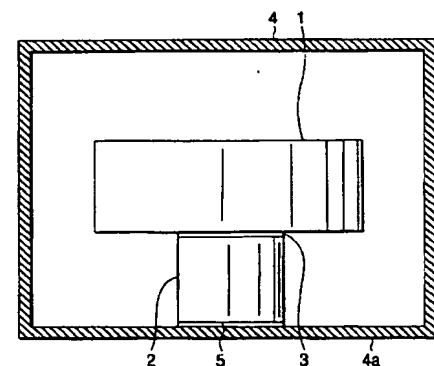
(74) Representative:

Grünecker, Kinkeldey,
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) A dielectric material, a method for producing the same and a dielectric resonator device comprising same

(57) Dielectric materials are disclosed that are based on BaO-ZnO-Ta₂O₅ represented by the formula Ba(Zn_{1/3}Ta_{2/3})O₃. Ba has been partly replaced by K and either Zn or Ta has been replaced by at least one element selected from Mg, Zr, Ga, Ni, Nb, Sn. The dielectric materials have a relatively high permittivity, a small absolute value of the temperature coefficient of resonance frequency, and a high unloaded quality factor. A method for producing the dielectric materials is also disclosed which includes mixing given amounts of starting materials, such as, for example, BaCO₃, ZnO, Ta₂O₅, K₂CO₃, MgCO₃, SnO₂ or ZrO₂, compacting the mixture to produce a compact, sintering the compact in an oxidizing atmosphere such as, for example, air, at 1,400 to 1,600°C, more preferably at 1,550 to 1,600°C for 2 hours, and then heating the sintered compact at a temperature lower than the sintering temperature by from 50 to 250°C, e.g., by 100°C, for at least 12 hours, preferably for 24 hours. A dielectric resonator comprising the dielectric material of the present invention is also disclosed.

FIG. 4



Description

This application claims the benefit of Japanese patent application No. Hei. 8-301202, filed October 25, 1996, and No. Hei. 9-191868, filed July 1, 1997, which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION**Field of the Invention**

The present invention relates to dielectric materials of excellent quality that have a relatively high permittivity (hereinafter referred to as ϵ_r) in a high frequency region, a small absolute value of the temperature coefficient of resonance frequency (hereinafter referred to as τ_f of f_0), and a high unloaded quality factor (hereinafter referred to as Q_u). The dielectric materials of the invention can be used in applications such as multilayer circuit boards, and, in particular, high-frequency resonators and filters. This invention further relates to processes for producing the dielectric materials.

Discussion of the Related Art

Dielectric materials based on BaO-ZnO-Ta₂O₅ or BaO-MgO-Ta₂O₅ are frequently used in high-frequency applications. Such dielectric materials for use in high-frequency applications must satisfy the following requirements:

- (i) a high ϵ_r ;
- (ii) a small absolute value of τ_f ; and
- (iii) a high Q_u in a high-frequency region.

The dielectric materials based on BaO-ZnO-Ta₂O₅ or BaO-MgO-Ta₂O₅ are oxides represented by the empirical formula Ba(Zn_{1/3}Ta_{2/3})O₃ or Ba(Mg_{1/3}Ta_{2/3})O₃, respectively, that have a perovskite crystal structure. These oxides are generally referred to as BZT and BMT for short. Although BZT and BMT materials are excellent dielectric materials having a high Q_u , there is a need for a dielectric material having an even higher Q_u because these dielectric materials are increasingly used in a higher-frequency region, from the microwave to the sub-millimeter wavelength region. In addition, these dielectric materials generally are produced by complex and industrially undesirable processes, which include sintering at high temperatures exceeding 1,600°C, sintering for a prolonged period, or sintering by ultrahigh-rate heating (see, for example, JP-B-6-25023, JP-A-4-224161, and JP-B-3-51242). (Here, "JP-B" and "JP-A" refer to an "examined Japanese patent publication" and an "unexamined published Japanese patent application," respectively.) Moreover, some trials of adding additives to these dielectric materials in order to improve sintering properties (see, for example, JP-B-1-18523 and JP-B-3-34164).

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a dielectric material and method for producing the same that substantially obviates one or more of the problems due to the limitations and disadvantages of the related art.

An object of the present invention is to provide dielectric materials that have a relatively high ϵ_r , of 20 or higher, and an absolute τ_f value, as small as 10 ppm/°C or below, and in which the product of Q_u as determined by Resonant Cavity Method (TE₀₁₈ mode) and f_0 (i.e., $Q_u \times f_0$) is 20,000 GHz or larger, and preferably 40,000 GHz or larger. (See H. Sreemoolandhan and M. T. Sebastian, "Dielectric Ceramic Materials for Microwave Resonator Applications", Metals Materials And Processes, 1995, Vol. 7, No. 4, pp. 251-266).

Another object of the present invention is to provide methods of manufacturing the above dielectric materials.

Another object of the present invention is to provide a dielectric resonator utilizing the dielectric material of the present invention.

To achieve these and other advantages, and in accordance with the purpose of the present invention, as embodied and broadly described, in a first aspect of the present invention there is provided a dielectric material including a complex oxide having a perovskite crystal structure and having a formula Ba(Q _{α} Y _{β} Z _{γ})O₃, wherein O is an Oxygen, Q is a metal, Y is a metal and Z is a metal; the dielectric material also optionally including A_pTaO_q, wherein A is an element selected from a group consisting of K, Li and Na.

In a second aspect of the present invention, there is provided a dielectric resonator, including a dielectric resonator element including complex oxide having a perovskite crystal structure and having a formula Ba(Q _{α} Y _{β} Z _{γ})O₃, wherein O is an Oxygen, Q is a metal, Y is a metal and Z is a metal; the dielectric material also optionally including A_pTaO_q, wherein A is an element selected from a group consisting of K, Li and Na; a metal casing enclosing the dielectric resonator element; and an insulating holder member attached to the dielectric resonator with a heat-resistive adhesive layer.

In a third aspect of the present invention, there is provided a dielectric material including a complex oxide having a perovskite crystal structure, wherein metallic elements are selected from a group consisting of Ba, Zn, Ta, and K.

In a fourth aspect of the present invention, there is provided a dielectric material including a complex oxide having a perovskite crystal structure, wherein metallic elements are selected from a group consisting of Ba, Zn, Ta, and K; and wherein at least either of the Zn or the Ta are at least partly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.

In a fifth aspect of the present invention, there is provided a dielectric material including between 80.0 and 99.9 mol% $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and between 0.1 and 20.0 mol% K_pTaO_q , wherein p is between 0.60 and 2.00.

In a sixth aspect of the present invention, there is provided a method of producing a dielectric material, wherein the dielectric material includes a complex oxide having a perovskite crystal structure, wherein metallic elements of the complex oxide are selected from a group consisting of Ba, Zn, Ta, and K as metallic elements, wherein the method includes the steps of mixing a barium compound, a zinc compound, a tantalum compound and a potassium compound to produce a mixture, wherein each of the compounds is either an oxide or a compound changing into an oxide upon heating; compacting the mixture to produce a compact; sintering the compact at a sintering temperature of between 1,300 and 1,650°C; and heat-treating the compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for at least 12 hours.

In a seventh aspect of the present invention, there is provided a method of producing a dielectric material including a complex oxide having a metallic element selected from a group consisting of Ba, Zn, Ta, and K and having a perovskite crystal structure, wherein at least either of the Zn or the Ta is at least partly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni; wherein the method includes the steps of mixing a barium compound, a zinc compound, a tantalum compound, a potassium compound and a compound of the at least one element that is either an oxide or a compound changing into an oxide upon heating to create a mixture; compacting the mixture to form a compact; sintering the compact at a sintering temperature of between 1,300 and 1,650°C; and heat-treating the compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for at least 12 hours.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

Additional features and advantages of the present invention will be set forth in the description which follows, and will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure and process particularly pointed out in the written description as well as in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention that together with the description serve to explain the principles of the invention.

In the drawings:

Fig. 1 illustrates the correlation between p in K_pTaO_q and $Q_u \times f_0$ as determined by Resonant Cavity Method;

Fig. 2 illustrates the correlation between p in K_pTaO_q and τ_f ;

Fig. 3 is a chart illustrating a comparison in X-ray diffraction patterns between dielectric material obtained in Experimental Example 1 and a dielectric material obtained in Experimental Example 10; and

Fig. 4 illustrates a dielectric resonator utilizing the dielectric material of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

In a first embodiment of the present invention, the dielectric material of the present invention includes complex oxides containing Ba, Zn, Ta, and K as metallic elements and having a perovskite crystal structure.

In a second embodiment of the present invention the dielectric material of the present invention includes complex oxides containing Ba, Zn, Ta, and K as metallic elements and having a perovskite crystal structure, wherein either Zn or Ta are partly or entirely replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.

In a third embodiment of the present invention there is provided a dielectric material including from 80.0 to 99.9 mol% $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and from 0.1 to 20.0 mol% K_pTaO_q (wherein $0.60 < p < 2.00$).

In a fourth embodiment of the present invention the dielectric material of the previous embodiment in which the pro-

portion of K_pTaO_q and the value of p are specified. In the dielectric materials of these two embodiments, at least either of the Zn and the Ta may have been partly or wholly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni. In this dielectric material, at least one element is preferably selected from the group consisting of Mg, Zr, Ga, Ni, Nb, and Sn.

5 $Ba(Zn_{1/3}Ta_{2/3})O_3$ is an oxide having a perovskite crystal structure. K_pTaO_q also may be an oxide having a perovskite crystal structure. Although the Ba in the dielectric materials described above may be partly replaced by the K, the results of analysis of these dielectric materials by X-ray diffractometry revealed that they have no crystal structure other than perovskite. It is presumed that the dielectric materials of the present invention has the same perovskite crystal structure as $Ba(Zn_{1/3}Ta_{2/3})O_3$.

10 In a fifth embodiment of the present invention there is provided a dielectric material described above wherein the element replacing either Zn or Ta is an element preferably selected from the group consisting of Mg, Zr, Ga, Ni, Nb, and Sn. These elements are advantageous in that Zn or Ta can be easily replaced, and a material having an intact perovskite crystal structure and excellent dielectric characteristics can be easily fabricated. Note also that the elements replacing Zn or Ta are not limited to those listed above. For example, Zn or Ta may be replaced by a rare earth element, such as, for example, Y. Like the dielectric materials in which Ba has been replaced by K, such dielectric materials with Zn or Ta replaced by another element have a perovskite crystal structure and, as X-ray diffractometry results show, have no other crystal phase.

15 In a sixth embodiment of the present invention, the K of K_pTaO_q is thought to be located in the position of the Ba of $Ba(Zn_{1/3}Ta_{2/3})O_3$, while the Ta is thought to be located in the position of the Zn or Ta of $Ba(Zn_{1/3}Ta_{2/3})O_3$. It is presumed that the dielectric material has a perovskite crystal structure consisting of $Ba(Zn_{1/3}Ta_{2/3})O_3$ containing K_pTaO_q of a perovskite structure. These dielectric materials can be obtained by a process where starting materials for $Ba(Zn_{1/3}Ta_{2/3})O_3$ are mixed with each other, together with a given amount of a potassium oxide or a potassium compound that changes into an oxide upon heating (for example, carbonate and oxalate), and the mixture is compacted, sintered, and then heat-treated.

20 If the value of p in K_pTaO_q is below 0.60, $Q_u \times f_0$ decreases considerably, sometimes to below 20,000 GHz, although ϵ_r and τ_f are almost satisfactory. In addition, such a small value of p tends to result in increased volatilization of potassium ions during sintering, yielding a sinter having a porous surface layer, which causes a decrease in $Q_u \times f_0$. On the other hand, if p exceeds 2.00, an excess of potassium is present, and there are cases where a potassium-containing crystal phase of a structure other than perovskite generates. The presence of this phase reduces $Q_u \times f_0$. An optimum value of p varies depending on the composition, and in the case of selecting BZT as a base composition, the value of p is preferably from 1.10 to 1.90, more preferably from 1.20 to 1.80. When p is within this range, a dielectric material having exceedingly high dielectric characteristics can be obtained having $Q_u \times f_0$ of 50,000 GHz or even 80,000 GHz or above, and having an absolute value of τ_f of 10 ppm/°C or even 1 ppm/°C or smaller, depending on the composition.

25 In the Resonant Cavity Method, one alternative method is to place the dielectric resonator (DR) exactly at the center of a cylindrical cavity with the same aspect ratio (D/L) as that of DR material as shown in Fig. 3a of H. Sreemoolandhan and M.T. Sebastian, "Dielectric Ceramic Materials for Microwave Resonator Applications", Metals Materials And Processes, 1995, Vol. 7, No. 4, pp. 251-266. A low loss material such as quartz (single crystal) may be used to support the DR. Two coupling loops are used to couple microwave to DRs which are symmetrically mounted.

30 If the proportion of K_pTaO_q is smaller than 0.1 mol% in the case of selecting BZT as a base composition, the dielectric material is unsatisfactory in that $Q_u \times f_0$, as determined by the Resonant Cavity Method is small, i.e. below 20,000 GHz. In addition, sintering properties may be reduced because of the reduced amount of the potassium compound (for example, carbonate and oxalate) incorporated as a starting material. On the other hand, if the proportion of K_pTaO_q exceeds 20 mol%, the value of $Q_u \times f_0$ decreases. The proportion of K_pTaO_q is preferably from 0.2 to 10 mol%, and more preferably from 0.5 to 10 mol%. When the proportion of K_pTaO_q is within this range, a dielectric material having excellent dielectric characteristics can be obtained, which has a high ϵ_r , an absolute τ_f value of 10 ppm/°C or even 5 ppm/°C or less, and a $Q_u \times f_0$ of 40,000 GHz or larger. Furthermore, even when the proportion of K_pTaO_q is as small as between approximately 2.0 and 3.0 mol%, a dielectric material having exceedingly high dielectric characteristics can be obtained as long as p is 1.20 or larger. As shown in the working examples mentioned below, it is confirmed that the dielectric materials of the present invention show excellent sintering properties and dielectric characteristics due to the addition of K_pTaO_q , while the optimum addition amount and p value are different slightly depending on the base composition.

35 In the seventh embodiment of the present invention there is provided a method of producing the dielectric material of the present invention that includes using complex oxides containing Ba, Zn, Ta, and K as metallic elements and having a perovskite crystal structure. This method includes mixing a barium compound, a zinc compound, a tantalum compound, and a potassium compound wherein each compound is either an oxide or a compound changing into an oxide upon heating (for example, carbonate); subsequently compacting the resultant mixture; sintering the compact at 1,300 to 1,650°C; and then heat-treating the sintered compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for 12 hours or longer.

40 In an eighth embodiment of the present invention, there is provided a method of the present invention is a process

for producing a dielectric material that includes complex oxides containing Ba, Zn, Ta, and K as metallic elements and having a perovskite crystal structure in which either Zn or Ta has been partly or wholly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni. This method includes mixing a barium compound, a zinc compound, a tantalum compound, a potassium compound, and a compound of at least one element where each is either an oxide or a compound changing into an oxide upon heating (e.g., carbonate), subsequently compacting the resultant mixture, sintering the compact at 1,300 to 1,650°C, and then heat-treating the sintered compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for 12 hours or longer.

If the sintering is conducted at a temperature lower than 1,300°C, a sufficiently densified sinter cannot be obtained, resulting in an insufficient improvement in Q_u . If the sintering is conducted at a temperature exceeding 1,650°C, the volatilization of potassium ions becomes more severe, tending to result in a sinter having a porous surface layer and an insufficient improvement in Q_u . The sintering temperature is therefore preferably from 1,350 to 1,600°C, more preferably from 1,400 to 1,600°C.

For densification, the sintering temperature is preferably 1,500°C or higher, more preferably 1,550°C or higher. Although sintering temperatures less than 1,600°C are effective in reducing the volatilization of potassium ions, temperatures lower than 1,600°C by at least 5°C, and preferably at least 10°C, are more effective. By sintering at a temperature in the range specified above, densification proceeds sufficiently, and volatilization of potassium ions is reduced to a low level. Thus, a dielectric material having excellent performance can be obtained. Although the period of sintering is not particularly limited, it is preferably between 1 and 4 hours, more preferably about 2 hours. The atmosphere for the sintering may be an oxidizing atmosphere, for example, air, or a reducing atmosphere containing hydrogen.

If the heat treatment is conducted at a relatively high temperature that is lower than the sintering temperature by less than 50°C, coarse grains are likely to generate because of enhanced grain growth, and an inhomogeneous material is likely to result. If the heat treatment is conducted at a relatively low temperature (lower than the sintering temperature by more than 250°C), the dielectric material does not acquire a long-period superlattice crystal structure, resulting in an insufficient improvement in Q_u . The temperature for the heat treatment is preferably 70 to 200°C lower than the sintering temperature, but more preferably 70 to 150°C lower and further preferably still by from 80 to 150°C lower. By conducting the heat treatment at a temperature lower than the sintering temperature by, for example, about 100°C, a dielectric material having a superlattice structure can be easily obtained.

The heat treatment is conducted in an oxidizing atmosphere. For example, air can be used as an atmosphere. Use of air as the atmosphere for the heat treatment is preferred because it requires neither a special procedure nor any special equipment. However, an oxidizing atmosphere in which the partial pressure of oxygen is higher than that in the air is preferred from the standpoint of dielectric properties, because use of this atmosphere yields a dielectric material with a better Q_u . If the heat treatment is conducted for a period less than 12 hours, it is impossible to convert a large proportion of the crystal structure into a superlattice structure, resulting in an insufficient improvement in Q_u . In order to have sufficient conversion into a superlattice structure, the period of the heat treatment is preferably 15 hours or longer, more preferably 18 hours or longer. A heat treatment period of 24 hours is sufficient. Although an even longer period, such as, for example, 48 hours may be used, such long-term heat treatment is only minimally effective from the standpoint of performance improvement.

The reasons why the replacement of Ba by K in complex oxides having perovskite crystal structure represented by a BZT dielectric material results in an improvement in the Q_u of the material are not yet clear. One possible explanation is that the BZT dielectric material, having a perovskite crystal structure, forms a solid solution with K_pTaO_q which also has a perovskite crystal structure, whereby the BZT dielectric material acquires a longer-period superlattice crystal structure and hence a high Q_u . Another possible explanation is that where K_pTaO_q having an irregular composition exists in the crystal structure, holes also are regularly located to form a superlattice structure, and the holes facilitate the movement of ions and atoms during sintering, accelerating densification. Due to this densification-accelerating effect, densification can be easily accomplished in producing BZT materials which have until now been produced through long-term sintering, or sintering by ultrahigh-rate heating, from substances having poor suitability for sintering.

In the ninth embodiment of the present invention, there is provided a dielectric resonator as shown in Fig. 4 including the dielectric material of the present invention. The resonator body 1 of a circular or rectangular shape in cross section is bonded to one end of holding member 2 by means of, for example, an epoxy resin type adhesive. The integrated resonator body 1 and holding member 2 are contained in the inside of metal container 4 of a cylindrical shape the both end surface of which are sealed up. One end of the holding member 2 is fixed and bonded to the center of the bottom surface 4a of the metal container 4 by means of PTFE.

The present invention will be further explained by reference to Experimental Examples, although the invention should not be construed as being limited thereto.

EXPERIMENTAL EXAMPLES 1 TO 48*(1) Production of Dielectric Materials*

Commercial BaCO_3 , ZnO (or any of the other oxides discussed below), Ta_2O_5 , and K_2CO_3 powders were mixed in various proportions, creating the compositions shown in Tables 1, 2, 3 and 4 under Experimental Examples 1 to 48. Each resultant composition was placed in a ball mill, and ethanol was then added thereto to conduct wet milling. In Tables 1 to 4, the proportions of all the ingredients are given in terms of oxide amounts. In place of ZnO and Ta_2O_5 , (1) MgO was incorporated in Experimental Examples 13, 27 and 36-39; (2) ZrO_2 was incorporated in Experimental Examples 14, 32 and 33 in addition to ZnO ; (3) SnO_2 was incorporated in Experimental Example 15; (4) NiO was incorporated in Experimental Examples 28 and 29, (5) Ga_2O_3 was incorporated in Experimental Examples 30 and 31; (6) Nb_2O_5 was incorporated in Experimental Examples 34 and 35; and (7) MgO and SnO_2 were incorporated in Experimental Examples 40-48. In Experimental Examples 11 and 12, Na_2CO_3 and Li_2CO_3 , respectively, were used in place of K_2CO_3 .

The slurries obtained by wet milling were dried and then calcined at $1,100^\circ\text{C}$ for 2 hours. A wax binder, a mixing/dispersing agent including a polycarboxylic acid and an amine, and ethanol were added to each resultant calcined powder. The mixtures were pulverized and homogenized with a ball mill. Subsequently, the slurries obtained were dried, granulated, and then compacted at a pressure of 1 GPa into a cylindrical form having a diameter of 23 mm and a thickness of 12 mm. The cylindrical compacts were subjected to cold isostatic pressing (CIP) at a pressure of 15 GPa, and then sintered for 2 hours in an air atmosphere at $1,600^\circ\text{C}$ in Experimental Examples 24 and 27 to 48, at $1,650^\circ\text{C}$ in Experimental Example 25, at $1,700^\circ\text{C}$ in Experimental Example 26, and at $1,550^\circ\text{C}$ in other Experimental Examples. Subsequently, the temperatures of the sintered compacts were lowered to $1,450^\circ\text{C}$, at which the sintered compacts were heat-treated for 24 hours.

(2) Evaluation of Dielectric Characteristics

The dielectric materials thus obtained were subjected to surface grinding or mirror polishing with a resin-bonded grindstone having a grain size of 200. The ground dielectric materials were examined for ϵ_r , Q_u , and τ_f by the Hakki and Coleman method (See Denesh C. Dube, Rudolf Zurmuhlen, Andrew Bell and Nava Setter, "Dielectric Measurements on High-Q Ceramics in the Microwave Region" *J. Am. Ceram. Soc.*, 80[5] 1095-1100) (TE_{011} mode) or Resonant Cavity Method ($\text{TE}_{01\delta}$ mode) at a frequency of 3 to 6 GHz (temperature range: 25 - 80°C). The results obtained are shown in Tables 5, 6, 7 and 8. In these Tables, the results concerning dielectric loss properties are given in terms of $Q_u \times f_0$. Since f_0 varies slightly with the measurement for determining Q_u , the product of Q_u and f_0 is used for a more precise expression of dielectric loss. In Tables 1 to 8, the "A" in A_pTaO_q represents an alkali metal, i.e. K, Na, or Li. In Tables 5, 6, 7 and 8, grinding refers to surface grinding and polishing refers to mirror polishing.

In the Hakki and Coleman method, the dielectric specimen is short-circuited (touched) by two conducting plates on both sides. Two small antennas are positioned in the vicinity of the specimen to couple power in and out of the resonator.

The results are given in Tables 5 to 8. The dielectric material obtained in Experimental Example 2, where the proportion of K_pTaO_q was as small as 0.25 mol% (although p was 1.00), had an exceedingly small absolute value of τ_f and a somewhat small $Q_u \times f_0$ value of about 30,000 GHz. However, this dielectric material is a great improvement in both $Q_u \times f_0$ and τ_f as compared to the potassium-free dielectric material obtained in Experimental Example 1. The dielectric materials obtained in Experimental Examples 3, 4, 8 to 10, 13 to 16, 21 to 35, 37-39 and 41-48, where p was between 1.00 and 1.70 and the proportion of K_pTaO_q was 0.5 mol% or larger, had excellent dielectric characteristics with a $Q_u \times f_0$ of from 37,700 to 143,700 GHz, except for the dielectric material obtained in Experimental Example 26 through sintering at $1,700^\circ\text{C}$. In particular, in case of selecting BZT as a base composition, the dielectric materials obtained in Experimental Examples 9, 10, 14-16, 24-26 and 28-35, where p was between 1.25 to 1.70, had even higher dielectric characteristics, with a $Q_u \times f_0$ ranging from 71,100 to 112,600 GHz.

On the other hand, the dielectric materials obtained in Experimental Examples 1, 36 and 40, which contained no potassium, had considerably worse dielectric characteristics, with an exceedingly small $Q_u \times f_0$ value, compared to the system having the same base material and containing potassium. That is, as is clear from the composition between Experimental Examples 1 and 24, Experimental Examples 36 and 27, and Experimental Examples 40 and 47, the values of $Q_u \times f_0$ in the system where potassium was added were improved regardless of the base composition, while the optimum addition amount and p value were slightly different depending on the base composition. The dielectric material obtained in Experimental Example 5, where p was 0.50, had insufficient performance with a value of $Q_u \times f_0$ in the $\text{TE}_{01\delta}$ mode (note that hereinafter all values of $Q_u \times f_0$ were determined in the $\text{TE}_{01\delta}$ mode) of 14,300 GHz, although the absolute values of τ_f were small. The dielectric material obtained in Experimental Example 17, where p was 2.00, had an exceedingly small $Q_u \times f_0$ value of less than 5,000 GHz and a relatively low ϵ_r , although the absolute value of τ_f was very

small. The dielectric material obtained in Experimental Example 18, where p was 3.00, could not be tested for dielectric characteristics because its resonance was weak. The dielectric materials obtained in Experimental Examples 19 and 20, where p was 4.00 to 5.00, respectively, developed cracks during sintering and hence had no measured characteristics.

The dielectric characteristics of the dielectric materials obtained in Experimental Examples 9 and 24 to 26, which had been obtained from the same composition through sintering at different temperatures, were as follows. The dielectric material of Experimental Example 24, which had been obtained through sintering at 1,600°C, had the largest value of $Q_U \times f_0$, which was higher than 100,000 GHZ. The dielectric material of Experimental Example 9, which had been obtained through sintering at 1,550°C, also had a high $Q_U \times f_0$ that exceeded 90,000 GHZ. On the other hand, the dielectric material of Experimental Example 26, which had been obtained through sintering at a relatively high temperature of 1,700°C, had a drawback in that the sinter had suffered surface melting. Furthermore, the dielectric material of Experimental Example 25, which had been obtained through sintering at 1,650°C, had a drawback in that the surface of the sinter had developed minute cracks probably due to the volatilization of potassium, although the dielectric material had a high $Q_U \times f_0$. These results indicate that the preferred range of the sintering temperature is from 1,550 to 1,600°C.

The results given in Tables 5 to 8 further show that by replacing Zn or Ta either in part or entirely with any of the other elements specified above, τ_f can be regulated to a desired value to some degree while still maintaining a high $Q_U \times f_0$, as in the dielectric materials obtained in Experimental Examples 14, 28 to 35 and 41-45. Specifically, by replacing part of Zn and Ta by Zr (Experimental Examples 14, 32, and 33) or replacing part of Ta by Nb (Experimental Examples 34 and 35), τ_f can be shifted to the positive side by values corresponding to the replacement amounts. By replacing part of Zn by Ni (Experimental Examples 28 and 29) or replacing part of Zn and Ta with Ga (Experimental Examples 30 and 31), τ_f can be shifted to the negative side by values corresponding to the replacement amounts. Further, τ_f can be controlled by adjusting the ratio Mg, Sn and Ta as in Experimental Examples 27 and 41-45.

It is also possible to regulate ϵ_r to a desired value to some degree while maintaining a high $Q_U \times f_0$ by replacing either Zn or Ta entirely with any of the other elements enumerated above, as in the dielectric materials obtained in Experimental Examples 13, 27, 37-39 and 41-48. Specifically, the results for Experimental Examples 13, 27 and 37-39 show that ϵ_r can be shifted by entirely replacing Zn with Mg. By replacing entire of Zn and part of Ta by Mg and Sn (Experimental Examples 41-48), ϵ_r can be shifted. In the present invention, part of Zn and Ta may be replaced by an element having a different valence, for example, Zr or Ga. With this replacement, a dielectric material having excellent performance can also be obtained.

The dielectric materials obtained in Experimental Examples 11 and 12 had an exceedingly low $Q_U \times f_0$. In these experiments another alkali metal, i.e., Na or Li, was used in place of K as the element replacing Ba. Each of these dielectric materials had a p of 1.44 and the proportion of A_pTaO_q was 2.50 mol%, which was in the preferred range. Thus, only K produces the desired effect, and using Na or Li, which are also alkali metals, produces no effect. With respect to the influence of surface finishing, such as surface grinding or mirror polishing, the test pieces which had undergone mirror polishing seemed to have slightly larger values of $Q_U \times f_0$, with some exceptions.

(3) Correlation between p and $Q_U \times f_0$ or τ_f

Fig. 1 shows the correlation between p and $Q_U \times f_0$ in the dielectric materials shown in Tables 5 and 6, where the base composition was $Ba(Zn_{1/3}Ta_{2/3})O_3$, p was in the range of between 0.50 and 2.00, and the proportion of K_pTaO_q was 2.50. These represent the dielectric materials obtained in Experimental Examples 5 to 10, 16, and 17. The correlation between p and τ_f in these dielectric materials is shown in Fig. 2. As shown in Fig. 1, $Q_U \times f_0$ reached a maximum when p was around 1.20 to 1.40, and $Q_U \times f_0$ decreased abruptly as p decreased to below 1.00 or increased beyond 1.70. As shown in Fig. 2, when p was in the range of between 1.20 and 1.70, τ_f was very satisfactory, with its absolute value below 1.0. Although the absolute value of τ_f increased with reducing p , it was still a very small value even when p was 2.00. As in Experimental Examples 13, 27, 37 and 38, in the case when K_pTaO_q was added to the base material other than BZT, $Q_U \times f_0$ varied depending on the value of p and had a maximum value when p was from 1 to 2, while the optimum value of p is different from that of BZT base material.

(4) Comparison in X-ray Diffraction Pattern between a Dielectric Material Containing K in place of Ba and a Dielectric Material not Containing K

Fig. 3 shows a comparison in X-ray diffraction patterns between the dielectric material obtained in Experimental Example 1, which did not contain K, and the dielectric material obtained in Experimental Example 10, where p was 1.44 and the proportion of K_pTaO_q was 2.50 mol%. Fig. 3 shows that no crystal phase other than perovskite was formed even in the dielectric material of Experimental Example 10, where Ba had been partly replaced by K, although the peaks in the diffraction pattern shifted slightly due to the formation of a solid solution containing K_pTaO_q .

(5) *Measurement of Density and Degree of Shrinkage*

The dielectric materials obtained by the method described above were examined for density and the degree of shrinkage by the following methods.

(i) Density: Archimedes' method

(ii) Degree of shrinkage: $\{[(\text{outer diameter of compact before CIP}) - (\text{outer diameter of sinter})] / (\text{outer diameter of compact before CIP})\} \times 100(\%)$

The results obtained are given in Tables 9, 10 and 11 and show the following. The dielectric materials did not greatly differ in density, except for the dielectric material obtained in Experimental Example 18, which could not be tested for dielectric characteristics because of its weak resonance and the dielectric material obtained in Experimental Example 40 where potassium was not added. With respect to the degree of shrinkage, the potassium-free dielectric material obtained in Experimental Example 1 had a rather small value. This is because the BZT material was difficult to sinter. The material also was difficult to sufficiently densify by an ordinary sintering technique without using a sintering aid. The dielectric material obtained in Experimental Example 13, 27 and 36-48, where Zn had been replaced by Mg, had a high degree of shrinkage because the MgO used as a starting material was a fine and bulky powder. The dielectric materials obtained in the Experimental Examples other than Experimental Examples 1, 13, 27 and 36-48 did not greatly differ in their degree of shrinkage. In these dielectric materials, the degree of shrinkage seemed to have no correlation with $Q_u \times f_0$.

In the dielectric materials obtained in Experimental Examples 9 and 24 to 26 from the same composition through sintering at different temperatures, higher sintering temperatures resulted in lower densities. This is because as the sintering temperature increases, potassium becomes more volatile and, as a result, a porous layer is likely to form on the periphery of the sinter. The decrease in density with increasing sintering temperature may also be attributable to the inhibition of densification due to the growth of crystal grains. These measurement results also support the preferred sintering temperature range of between 1,550 and 1,600°C, similar to using method (2) above.

(6) *Analysis for Potassium Content*

The dielectric materials obtained in Experimental Examples 8 and 23 were analyzed for elemental composition by ICP spectrometry. The results obtained are shown in Table 12, where each theoretical value is the same as the proportion of the ingredient actually mixed. Each number given in parentheses under "K" represents the proportion of volatilized potassium.

From the results given in Table 12, including the measured values of potassium content, and from the results of measurement of dielectric characteristics, it is presumed that in a compact containing potassium in an amount ($p > 1.00$) larger than the stoichiometric amount, the excess potassium volatilizes in the sintering step to almost stoichiometrically yield KTaO_3 ($p = 1.00$), and the dielectric material thus obtained has an especially high $Q_u \times f_0$.

(7) *An Example of Dielectric Resonator Prepared by Using Dielectric Material of the Invention*

Fig. 4 illustrates an example of a dielectric resonator providing resonator body 1 comprising the dielectric material of the present invention. The resonator body 1 is bonded to one end of holding member 2 by means of, for example, an epoxy resin type adhesive. The integrated resonator body 1 and holding member 2 are contained in the inside of metal container 4 of a cylindrical shape the both end surface of which are sealed up. One end of the holding member 2 is fixed and bonded to the center of the bottom surface 4a of the metal container 4 by means of PTTF.

As demonstrated above, the dielectric materials of present invention have a specific crystal structure, a relatively high ϵ_r , a small absolute value of τ_f , and a large value of $Q_u \times f_0$. The processes for production of these dielectric material is easy and uses no unusual complex or industrially disadvantageous sintering techniques, such as long-term sintering or sintering by ultrahigh-rate heating.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

Table 1

Experimental Example	Base Composition (wt%)						A _p TaO _q Ingredient (wt%)			
	BaO*	ZnO	MgO	ZrO ₂	SnO ₂	Ta ₂ O ₅	K ₂ O*	Na ₂ O*	Li ₂ O*	Ta ₂ O ₅
1	46.78	8.28	-	-	-	44.94	-	-	-	-
2	46.68	8.26	-	-	-	44.85	0.04	-	-	0.17
3	46.59	8.24	-	-	-	44.76	0.07	-	-	0.34
4	46.21	8.17	-	-	-	44.39	0.22	-	-	1.01
5	45.90	8.12	-	-	-	44.10	0.18	-	-	1.70
6	45.87	8.12	-	-	-	44.07	0.25	-	-	1.69
7	45.85	8.11	-	-	-	44.04	0.31	-	-	1.69
8	45.82	8.11	-	-	-	44.02	0.36	-	-	1.69
9	45.78	8.10	-	-	-	43.98	0.45	-	-	1.69
10	45.75	8.09	-	-	-	43.95	0.52	-	-	1.69
11	45.83	8.12	-	-	-	44.02	-	0.34	-	1.69
12	45.91	8.12	-	-	-	44.11	-	-	0.17	1.69

*Carbonic acid salt was used as starting material.

Table 2

Experimental Example	Base Composition (wt%)						A _p TaO _q Ingredient (wt%)			
	BaO*	ZnO	MgO	ZrO ₂	SnO ₂	Ta ₂ O ₅	K ₂ O*	Na ₂ O*	Li ₂ O*	Ta ₂ O ₅
13	47.70	-	4.18	-	-	45.82	0.54	-	-	1.76
14	46.11	7.59	-	2.22	-	41.86	0.52	-	-	1.70
15	45.98	7.32	-	-	4.07	40.41	0.52	-	-	1.70
16	45.70	8.09	-	-	-	43.91	0.61	-	-	1.69
17	45.66	8.08	-	-	-	43.86	0.72	-	-	1.68
18	45.49	8.05	-	-	-	43.70	1.08	-	-	1.68
19	45.33	8.02	-	-	-	43.55	1.43	-	-	1.67
20	45.17	7.99	-	-	-	43.39	1.78	-	-	1.67
21	44.85	7.93	-	-	-	43.09	0.73	-	-	3.40
22	43.87	7.76	-	-	-	42.15	1.09	-	-	5.13
23	42.88	7.59	-	-	-	41.20	1.46	-	-	6.87

*Carbonic acid salt was used as starting material.

Table 3

Experi- mental Example	Base Composition (wt%)								A _p TaO _q Ingredient (wt%)				
	BaO*	ZnO	MgO	NiO	Ga ₂ O ₃	ZrO ₂	SnO ₂	Nb ₂ O ₅	Ta ₂ O ₅	K ₂ O*	Na ₂ O*	Li ₂ O*	Ta ₂ O ₅
24	45.78	8.10	-	-	-	-	-	-	43.98	0.45	-	-	1.69
25	45.78	8.10	-	-	-	-	-	-	43.98	0.45	-	-	1.69
26	45.78	8.10	-	-	-	-	-	-	43.98	0.45	-	-	1.69
27	47.74	-	0.47	-	-	-	-	-	45.86	0.47	-	-	1.76
28	45.74	7.28	-	0.67	-	-	-	-	44.17	0.45	-	-	1.69
29	45.79	6.08	-	1.78	-	-	-	-	44.21	0.45	-	-	1.69
30	45.88	8.04	-	-	0.28	-	-	-	43.65	0.45	-	-	1.70
31	46.06	7.82	-	-	0.84	-	-	-	43.13	0.45	-	-	1.70
32	45.99	8.05	-	-	-	0.74	-	-	43.07	0.45	-	-	1.70
33	46.15	7.59	-	-	-	2.22	-	-	41.89	0.45	-	-	1.70
34	46.56	8.16	-	-	-	-	-	2.83	40.27	0.46	-	-	1.72
35	47.86	8.36	-	-	-	-	-	7.05	34.49	0.47	-	0.17	1.77

*Carbonic acid salt was used as starting material.

Table 4

Experimental Example	Base Composition (wt%)						A _p TaO _q Ingredient (wt%)			
	BaO*	ZnO	MgO	ZrO ₂	SnO ₂	Ta ₂ O ₅	K ₂ O*	Na ₂ O*	Li ₂ O*	Ta ₂ O ₅
36	48.82	-	4.28	-	-	46.90	-	-	-	-
37	47.77	-	4.18	-	-	45.90	0.38	-	-	1.77
38	46.72	-	4.09	-	-	44.89	0.76	-	-	3.54
39	46.63	-	4.09	-	-	44.80	0.94	-	-	3.54
40	49.06	-	3.65	-	7.23	40.06	-	-	-	-
41	47.84	-	3.98	-	2.35	43.65	0.46	-	-	1.72
42	47.91	-	3.78	-	4.70	41.42	0.46	-	-	1.73
43	47.98	-	3.57	-	7.08	39.18	0.46	-	-	1.73
44	48.06	-	3.37	-	9.45	36.93	0.46	-	-	1.73
45	48.13	-	3.16	-	11.84	34.68	0.46	-	-	1.73
46	48.62	-	3.62	-	7.17	39.70	0.19	-	-	0.70
47	46.95	-	3.50	-	6.93	38.34	0.90	-	-	3.38
48	44.63	-	3.32	-	6.58	36.43	1.90	-	-	7.14

*Carbonic acid salt was used as starting material.

Table 5

Experimental Example	Base Composition	A _p TaO _q Ingredient			Dielectric Properties					
		Value of p	A	Proportion (mol%)	ϵ_r	Qxf (GHz) 016/grinding	Qxf (GHz) 016/polishing	Qxf (GHz) 011/grinding	Qxf (GHz) 011/polishing	τ_f (ppm/°C)
1	Ba(Zn _{1/3} Ta _{2/3})O ₃	-	-	0.00	26.9	1500	-	1500	-	36.4
2	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	0.25	28.8	29700	-	20500	-	-0.6
3	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	0.50	28.8	42300	-	25300	-	1.5
4	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	1.50	28.6	48600	50100	24300	24400	2.3
5	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.50	K	2.50	29.8	14300	-	14300	-	10.0
6	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.70	K	2.50	29.5	20200	24100	20100	19700	5.5
7	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.85	K	2.50	29.5	18100	-	18800	-	2.4
8	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	2.50	29.5	48900	53300	24800	24900	2.0
9	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	29.3	93900	95400	27900	27700	-0.8
10	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	K	2.50	28.6	84800	85000	27300	27200	-0.3
11	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	Na	2.50	29.8	1400	-	1100	-	6.0
12	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	Li	2.50	28.6	4100	4000	3400	2900	0.3

Table 6

Experimental Example	Base Composition	A _p TaO _q Ingredient			Dielectric Properties					
		Value of p	A	Proportion (mol%)	ϵ_r	Qxf (GHz) 018/grinding	Qxf (GHz) 018/polishing	Qxf (GHz) 011/grinding	Qxf (GHz) 011/polishing	τ_f (ppm/°C)
13	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.44	K	2.50	24.2	97500	-	30100	-	8.2
14	Ba(Zr _{0.06} Zn _{0.31} Ta _{0.63})O ₃	1.44	K	2.50	31.4	98800	90600	26600	26200	8.5
15	Ba(Sn _{0.09} Zn _{0.30} Ta _{0.61})O ₃	1.44	K	2.50	28.6	88300	96400	27700	27800	-0.2
16	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.70	K	2.50	29.3	81300	79300	26900	26500	-0.7
17	Ba(Zn _{1/3} Ta _{2/3})O ₃	2.00	K	2.50	26.2	1000	4900	800	5700	-0.1
18	Ba(Zn _{1/3} Ta _{2/3})O ₃	3.00	K	2.50	could not be determined due to weak resonance					
19	Ba(Zn _{1/3} Ta _{2/3})O ₃	4.00	K	2.50	cracking occurred during sintering					
20	Ba(Zn _{1/3} Ta _{2/3})O ₃	5.00	K	2.50	cracking occurred during sintering					
21	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	5.00	29.0	37700	38000	20300	19500	4.7
22	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	7.50	28.6	55300	82000	28000	29500	1.4
23	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	10.0	29.1	64500	69200	26700	26900	6.6

Table 7

Experimental Example	Base Composition	A _p TaO _q Ingredient			Dielectric Properties					
		Value of p	A	Proportion (mol%)	ϵ_r	Qxf (GHz) 01δ/grinding	Qxf (GHz) 01δ/polishing	Qxf (GHz) 011/grinding	Qxf (GHz) 011/polishing	τ_f (ppm/°C)
24	Ba(2n _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	28.3	102900	-	29400	-	-1.1
25	Ba(2n _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	28.3	93300	-	27800	-	-0.7
26	Ba(2n _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	sinter surface melted					
27	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	24.9	111600	-	32600	-	8.2
28	Ba(Ni _{0.03} Zn _{0.30} Ta _{0.67})O ₃	1.25	K	2.50	28.5	88300	-	28100	-	-2.8
29	Ba(Ni _{0.08} Zn _{0.35} Ta _{0.67})O ₃	1.25	K	2.50	27.4	71100	-	27000	-	-4.2
30	Ba(Ga _{0.01} Zn _{0.31} Ta _{0.66})O ₃	1.25	K	2.50	28.8	112600	-	29600	-	-1.8
31	Ba(Ga _{0.03} Zn _{0.31} Ta _{0.65})O ₃	1.25	K	2.50	28.6	109000	-	29400	-	-3.2
32	Ba(Zr _{0.02} Zn _{0.31} Ta _{0.65})O ₃	1.25	K	2.50	28.8	85600	-	27700	-	1.5
33	Ba(Zr _{0.06} Zn _{0.31} Ta _{0.63})O ₃	1.25	K	2.50	30.8	89700	-	26700	-	9.3
34	Ba(Zn _{0.33} Nb _{0.07} Ta _{0.60})O ₃	1.25	K	2.50	29.6	94500	-	27300	-	2.5
35	Ba(Zn _{0.33} Nb _{0.17} Ta _{0.50})O ₃	1.25	K	2.50	29.8	95300	-	27400	-	3.4

Table 8

Experimental Example	Base Composition	A _p TaO _q Ingredient			Dielectric Properties					
		Value of p	A	Proportion (mol%)	ϵ_r	Qxf (GHz) 016/grinding	Qxf (GHz) 016/polishing	Qxf (GHz) 011/grinding	Qxf (GHz) 011/polishing	τ_f (ppm/°C)
36	Ba(Mg _{1/3} Ta _{2/3})O ₃	-	-	0	22.7	23700	-	18500	-	12.6
37	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.00	K	2.50	23.9	97800	-	31300	-	10.5
38	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.00	K	5.00	25.4	94700	-	30900	-	9.6
39	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.25	K	5.00	25.2	95800	-	31200	-	9.5
40	Ba(Sn _{0.13} Mg _{0.28} Ta _{0.57})O ₃	-	-	0	21.9	40800	-	22900	-	-3.4
41	Ba(Sn _{0.03} Mg _{0.32} Ta _{0.63})O ₃	1.25	K	2.50	25.5	70400	-	29500	-	2.7
42	Ba(Sn _{0.10} Mg _{0.30} Ta _{0.60})O ₃	1.25	K	2.50	24.4	113200	-	33000	-	1.9
43	Ba(Sn _{0.13} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	2.50	24.1	139400	-	34900	-	0.5
44	Ba(Sn _{0.20} Mg _{0.27} Ta _{0.53})O ₃	1.25	K	2.50	23.6	127000	-	33900	-	-5.2
45	Ba(Sn _{0.23} Mg _{0.25} Ta _{0.50})O ₃	1.25	K	2.50	23.1	114200	-	34100	-	-6.4
46	Ba(Sn _{0.13} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	1.00	24.1	116200	-	33000	-	-5.4
47	Ba(Sn _{0.13} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	5.00	23.7	143700	-	34300	-	-1.8
48	Ba(Sn _{0.13} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	10.0	24.0	103700	-	32300	-	1.3

Table 9

Experimental Example	Base Composition (wt%)	A _p TaO _q Ingredient			Density (g/cm ³)	Degree of shrinkage (%)
		Value of p	A	Proportion (mol%)		
1	Ba(Zn _{1/3} Ta _{2/3})O ₃	-	-	0.00	7.33	14.8
2	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	0.25	7.74	17.1
3	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	0.50	7.76	19.5
4	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	1.50	7.67	18.8
5	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.50	K	2.50	7.77	18.9
6	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.70	K	2.50	7.78	18.9
7	Ba(Zn _{1/3} Ta _{2/3})O ₃	0.85	K	2.50	7.79	19.5
8	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	2.50	7.79	19.1
9	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	7.78	18.7
10	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	K	2.50	7.75	18.4
11	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	Na	2.50	7.69	18.4
12	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.44	Li	2.50	7.65	18.2
13	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.44	K	2.50	7.44	22.0
14	Ba(Zr _{0.06} Zn _{0.31} Ta _{0.63})O ₃	1.44	K	2.50	7.64	17.9
15	Ba(Sn _{0.09} Zn _{0.30} Ta _{0.61})O ₃	1.44	K	2.50	7.65	18.0
16	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.70	K	2.50	7.72	18.5
17	Ba(Zn _{1/3} Ta _{2/3})O ₃	2.00	K	2.50	7.28	17.1
18	Ba(Zn _{1/3} Ta _{2/3})O ₃	3.00	K	2.50	7.07	17.9

Table 10

Experimental Example	Base Composition (wt%)	A _p TaO _q Ingredient			Density (g/cm ³)	Degree of shrinkage (%)
		Value of p	A	Proportion (mol%)		
19	Ba(Zn _{1/3} Ta _{2/3})O ₃	4.00	K	2.50	cracking occurred during sintering	
20	Ba(Zn _{1/3} Ta _{2/3})O ₃	5.00	K	2.50	cracking occurred during sintering	
21	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	5.00	7.67	20.1
22	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	7.50	7.48	18.7
23	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.00	K	10.0	7.37	19.1
24	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	7.68	18.1
25	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	7.60	17.8
26	Ba(Zn _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	7.56	**
27	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.25	K	2.50	7.37	23.7
28	Ba(Ni _{0.03} Zn _{0.30} Ta _{0.67})O ₃	1.25	K	2.50	7.63	17.7
29	Ba(Ni _{0.08} Zn _{0.25} Ta _{0.67})O ₃	1.25	K	2.50	7.60	17.5
30	Ba(Ga _{0.01} Zn _{0.33} Ta _{0.66})O ₃	1.25	K	2.50	7.52	18.0
31	Ba(Ga _{0.03} Zn _{0.32} Ta _{0.65})O ₃	1.25	K	2.50	7.40	17.8
32	Ba(Zr _{0.02} Zn _{0.33} Ta _{0.65})O ₃	1.25	K	2.50	7.66	18.1
33	Ba(Zr _{0.06} Zn _{0.31} Ta _{0.63})O ₃	1.25	K	2.50	7.69	18.4
34	Ba(Zn _{0.33} Nb _{0.07} Ta _{0.60})O ₃	1.25	K	2.50	7.41	17.3
35	Ba(Zn _{0.33} Nb _{0.17} Ta _{0.50})O ₃	1.25	K	2.50	7.24	17.0

** Sinter surface melted.

Table 11

Experimental Example	Base Composition (wt%)	A _p TaO _q Ingredient			Density (g/cm ³)	Degree of shrinkage (%)
		Value of p	A	Proportion (mol%)		
36	Ba(Mg _{1/3} Ta _{2/3})O ₃	-	-	0	7.23	20.7
37	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.00	K	2.50	7.53	23.9
38	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.00	K	5.00	7.43	23.8
39	Ba(Mg _{1/3} Ta _{2/3})O ₃	1.25	K	5.00	7.48	22.3
40	Ba(Sn _{0.15} Mg _{0.26} Ta _{0.57})O ₃	-	-	-	6.95	21.0
41	Ba(Sn _{0.05} Mg _{0.32} Ta _{0.53})O ₃	1.25	K	2.50	7.49	24.4
42	Ba(Sn _{0.10} Mg _{0.30} Ta _{0.50})O ₃	1.25	K	2.50	7.49	22.0
43	Ba(Sn _{0.15} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	2.50	7.41	22.4
44	Ba(Sn _{0.20} Mg _{0.27} Ta _{0.53})O ₃	1.25	K	2.50	7.39	22.8
45	Ba(Sn _{0.25} Mg _{0.25} Ta _{0.50})O ₃	1.25	K	2.50	7.39	22.1
46	Ba(Sn _{0.15} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	1.00	7.47	22.7
47	Ba(Sn _{0.15} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	5.00	7.31	21.9
48	Ba(Sn _{0.15} Mg _{0.28} Ta _{0.57})O ₃	1.25	K	10.0	7.19	22.5

Table 12

Experi- mental Example	Base composition	Value of p	Proportion of K_pTaO_q (mol%)	Elemental Composition (wt%)				
				K	Ba	Zn	Ta	O
8	$Ba(Zn_{1/3}Ta_{2/3})O_3$	1.00	2.50	Theoretical value	0.30	41.04	6.51	37.44
				Measured value	0.21(30.0)	40.10	6.22	-
23	$Ba(Zn_{1/3}Ta_{2/3})O_3$	1.00	10.0	Theoretical value	1.22	38.41	6.09	39.36
				Measured value	1.07(12.3)	37.70	5.81	-

Claims

1. A dielectric material comprising a complex oxide having a perovskite crystal structure and having a formula $Ba(Q_{\alpha}Y_{\beta}Z_{\gamma})O_{\delta}$, wherein O is an Oxygen, Q is a metal, Y is a metal and Z is a metal;
 5 the dielectric material also optionally comprising A_pTaO_q , wherein A is an element selected from a group consisting of K, Li and Na.
2. The dielectric material of claim 1, wherein δ equals 3.
- 10 3. The dielectric material of claim 2, wherein a sum of α , β and γ equals 1.
4. The dielectric material of claim 3, wherein Y is a zinc and Z is a tantalum.
5. The dielectric material of claim 4, wherein α equals 0.
- 15 6. The dielectric material of claim 5, wherein β equals 1/3 and γ equals 2/3.
7. The dielectric material according to one of the claims 1 to 3, wherein Q is an element selected from a group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.
- 20 8. The dielectric material according to one of the claims 1 to 3, wherein Q is an element selected from a group consisting of Mg, Zr, Ga, Ni, Nb, and Sn.
9. The dielectric material according to one of the claims 1 to 8, wherein an amount of A_pTaO_q is selected to result in a concentration of between 0.1 and 20.0 mol% A_pTaO_q and p is between 0.60 and 2.00.
- 25 10. The dielectric material according to one of the claims 1 to 8, wherein an amount of A_pTaO_q is selected to result in a concentration of between 0.1 and 15.0 mol% A_pTaO_q and p is between 1.00 and 2.00.
- 30 11. A dielectric resonator, comprising:
 - a dielectric resonator element comprising complex oxide having perovskite crystal structure and having a formula $Ba(Q_{\alpha}Y_{\beta}Z_{\gamma})O_{\delta}$, wherein O is an Oxygen, Q is a metal, Y is a metal and Z is a metal;
 - 35 the dielectric material also optionally comprising A_pTaO_q , wherein A is an element selected from a group consisting of K, Li and Na;
 - a metal casing enclosing the dielectric resonator element; and
 - 40 an insulating holder member attached to the dielectric resonator with a heat-resistive adhesive layer.
12. The dielectric resonator of claim 11, wherein δ equals 3.
13. The dielectric resonator of claim 12, wherein a sum of α , β and γ equals 1.
- 45 14. The dielectric resonator of claim 13, wherein Y is a zinc and Z is a tantalum.
15. The dielectric resonator of claim 14, wherein α equals 0.
- 50 16. The dielectric resonator of claim 13, wherein β equals 1/3 and γ equals 2/3.
17. The dielectric resonator according to one of the claims 11 to 13, wherein Q is an element selected from a group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.
- 55 18. The dielectric resonator according to one of the claims 11 to 13, wherein Q is an element selected from a group consisting of Mg, Zr, Ga, Ni, Nb, and Sn.
19. The dielectric resonator according to one of the claims 11 to 18, wherein an amount of A_pTaO_q is selected to result

in a concentration of between 0.1 and 20.0 mol% A_pTaO_q and p is between 0.60 and 2.00.

20. The dielectric resonator according to one of the claims 11 to 18, wherein an amount of A_pTaO_q is selected to result in a concentration of between 0.1 and 15.0 mol% A_pTaO_q and p is between 1.00 and 2.00.

21. A dielectric material comprising a complex oxide having a perovskite crystal structure, wherein metallic elements are selected from a group consisting of Ba, Zn, Ta, and K.

22. A dielectric material comprising a complex oxide having a perovskite crystal structure, wherein metallic elements are selected from a group consisting of Ba, Zn, Ta, and K; and wherein at least either of Zn and the Ta are at least partly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.

23. The dielectric material of claim 22, wherein at least either of the Zn and the Ta are at least partly replaced by at least one element selected from the group consisting of Mg, Zr, Ga, Ni, Nb, and Sn.

24. A dielectric material comprising between 80.0 and 99.9 mol% $Ba(Zn_{1/3}Ta_{2/3})O_3$ and between 0.1 and 20.0 mol% K_pTaO_q , wherein p is between 0.60 and 2.00.

25. A dielectric material comprising between 85.0 and 99.9% $Ba(Zn_{1/3}Ta_{2/3})O_3$ and between 0.1 and 15.0 mol% K_pTaO_q , and p is between 1.00 and 2.00.

26. The dielectric material according to one of the claims 24 or 25, wherein at least either of the Zn and the Ta are at least partly replaced by at least one element selected from a group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni.

27. A method of producing a dielectric material that comprises a complex oxide having a perovskite crystal structure, wherein metallic elements of the complex oxide are selected from a group consisting of Ba, Zn, Ta, and K as metallic elements, the method comprising the steps of:

mixing a barium compound, a zinc compound, a tantalum compound and a potassium compound to produce a mixture, wherein each of the compounds is either an oxide or a compound changing into an oxide upon heating;

compacting the mixture to produce a compact;

sintering the compact at a sintering temperature of between 1,300 and 1,650°C; and

heat-treating the compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for at least 12 hours.

28. A method of producing a dielectric material comprising a complex oxide having a metallic element selected from a group consisting of Ba, Zn, Ta, and K and having a perovskite crystal structure, wherein at least either of the Zn and the Ta is at least partly replaced by at least one element selected from the group consisting of Mg, Ca, Sr, La, B, Al, Ga, Ti, Zr, Hf, V, Nb, Si, Sn, Sb, Mn, Fe, Co, W, and Ni, the method comprising the steps of:

mixing a barium compound, a zinc compound, a tantalum compound, a potassium compound and a compound of the at least one element which each is either an oxide or a compound changing into an oxide upon heating to create a mixture;

compacting the mixture to form a compact;

sintering the compact at a sintering temperature of between 1,300 and 1650°C; and

heat-treating the compact at a temperature lower than the sintering temperature by from 50 to 250°C in an oxidizing atmosphere for at least 12 hours.

29. The method of claim 28, wherein the at least one element is selected from the group consisting of Mg, Zr, Ga, Ni,

EP 0 838 446 A1

Nb, and Sn.

30. The method of claim 28 or 29, wherein the sintering is conducted at a temperature of between 1,400 and 1,600°C.

5 **31.** The method according to one of the claims 28 to 30, wherein the heat treatment is conducted at a temperature lower than the sintering temperature by from 80 to 150°C.

32. The method according to one of the claims 28 to 31, wherein air is used as the oxidizing atmosphere.

10

15

20

25

30

35

40

45

50

55

FIG. 1

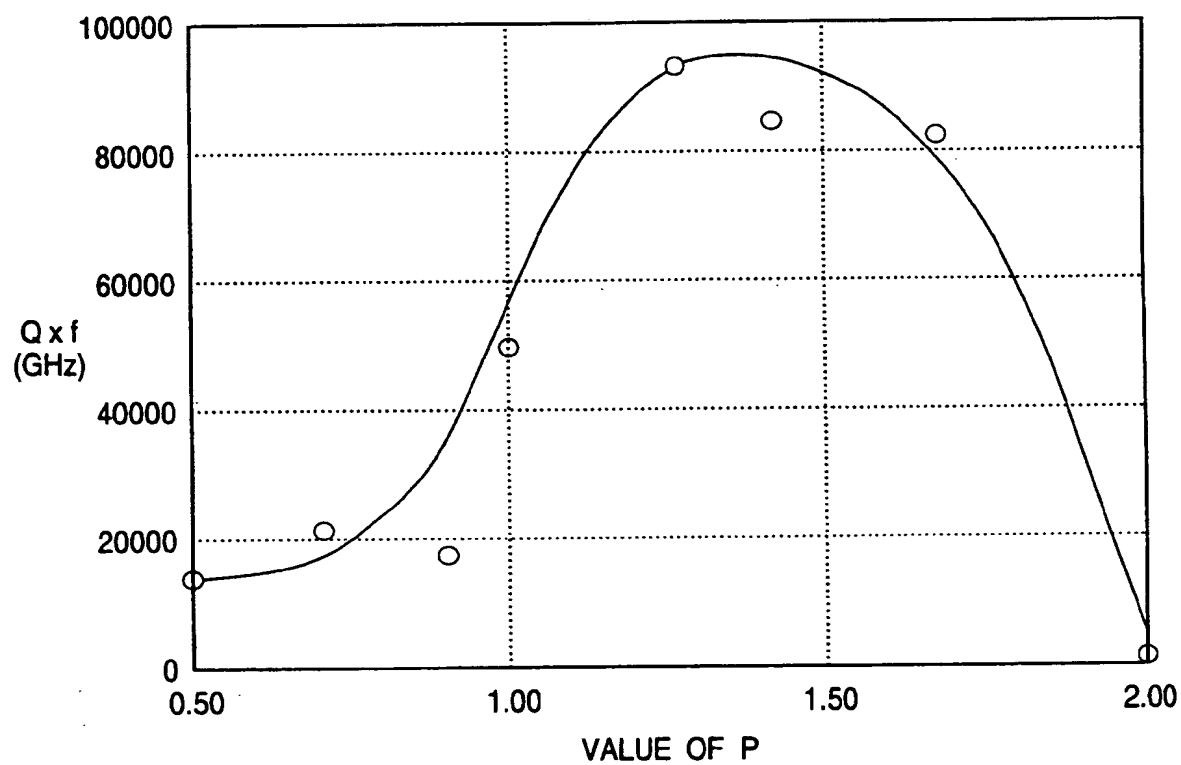


FIG. 2

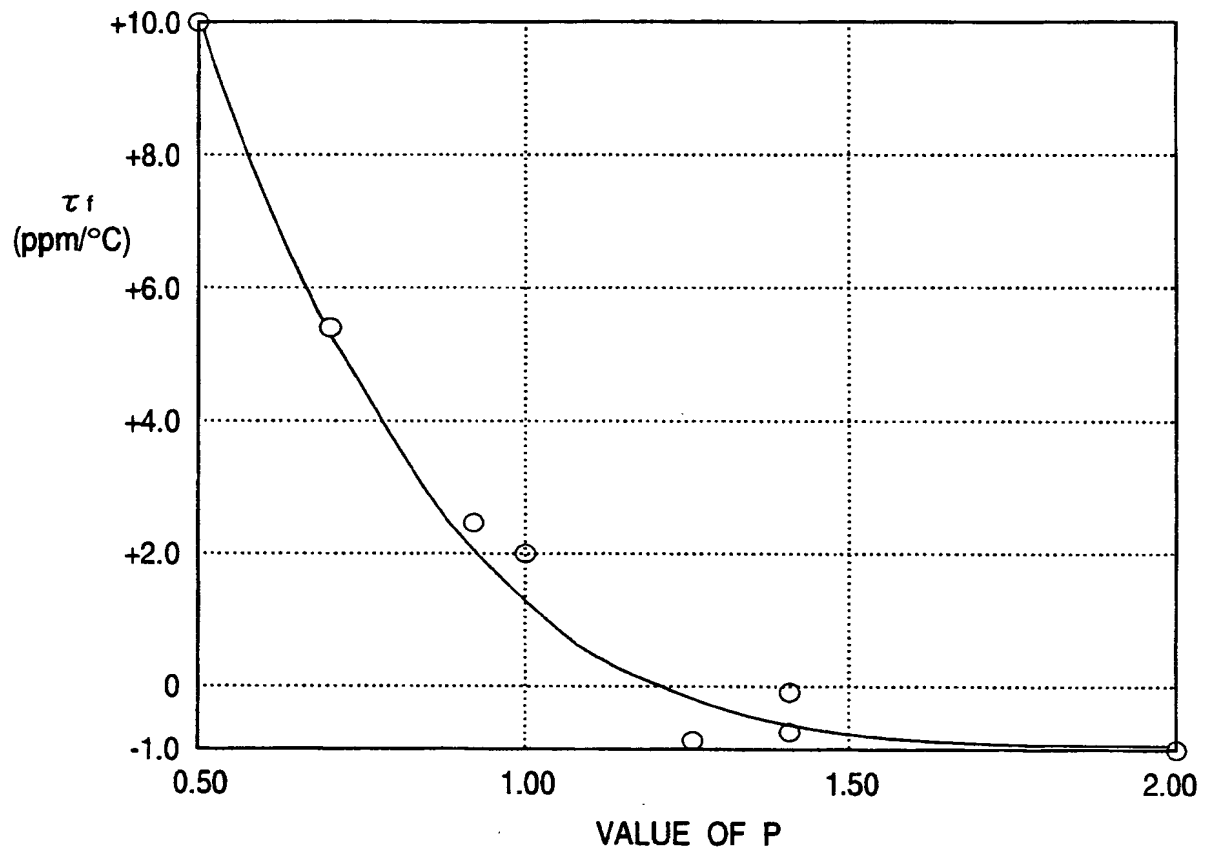


FIG. 3

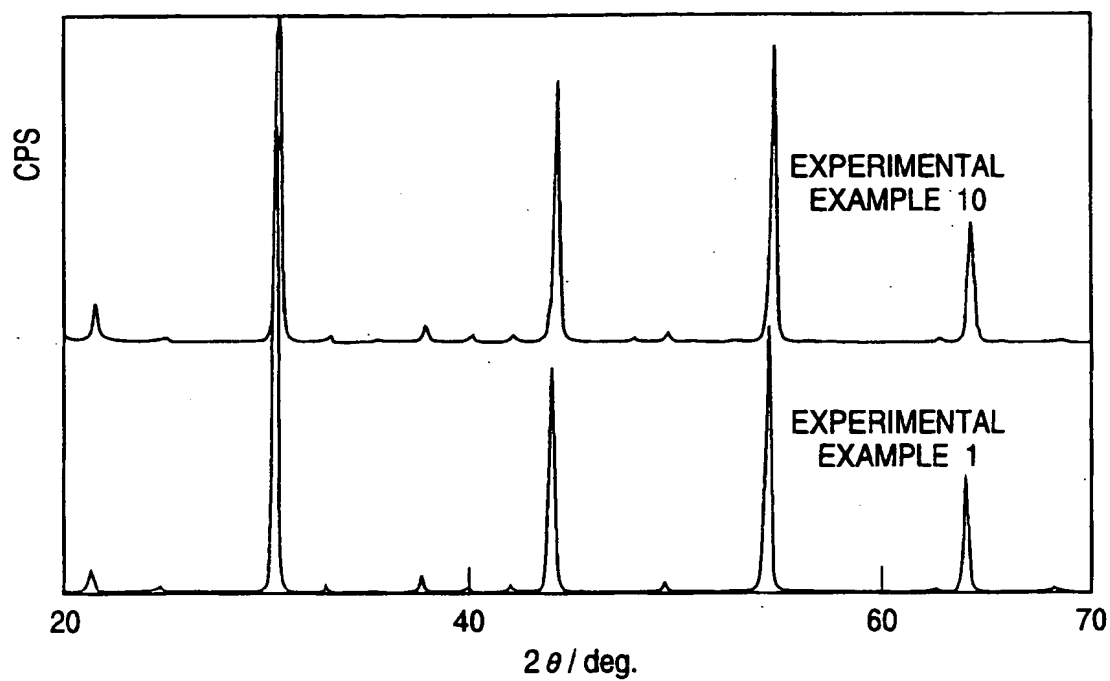
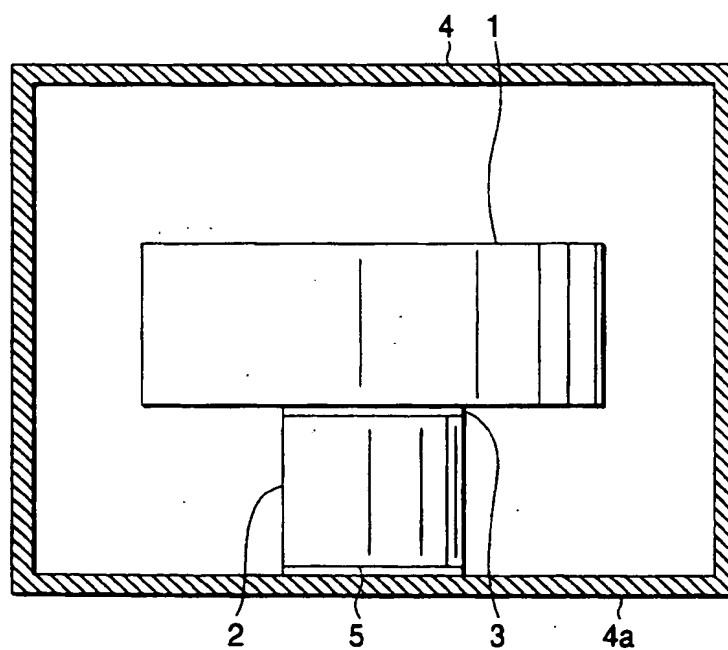


FIG. 4



EP 0 838 446 A1

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 8539

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	EP 0 369 768 A (SUMITOMO METAL MINING CO) * claims 1-4,8-10 * * page 2, line 13 - line 20 * * examples: table 2 * ---	1-8, 11-18, 21-23, 27-32 24-26	C04B35/495 H01P7/10
X A	KIM E S ET AL: "EFFECT OF NICKEL ON MICROWAVE DIELECTRIC PROPERTIES OF BA(MG1/3TA2/3)O3" JOURNAL OF MATERIALS SCIENCE, vol. 29, no. 3, 1 February 1994, pages 830-834, XP000429210 * page 830, left-hand column, line 1 - right-hand column, line 8 * ---	1-8, 11-18, 21-23, 27-29, 31,32 24-26	
X A	EP 0 545 775 A (RHONE POULENC CHIMIE) * page 1, line 1-11 * * examples 1,3 * * claims 5,13 * ---	1-8, 11-18, 21-23 24-29	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C04B H01P
X A	EP 0 639 541 A (NGK SPARK PLUG CO) * claims 1,6,14,15 * * page 7, line 6 - line 9 * * examples; table 1 * ---	1,2,7, 11,12, 17, 21-23, 27-30,32 3-6,8, 13-16, 18,24-26	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 1998	Examiner Rosenberger, J
CATEGORY OF CITED DOCUMENTS X particularly relevant if taken alone ✓ particularly relevant if combined with another document of the same category A technological background ○ non-written disclosure P intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P34C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 8539

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	KUNIO TOCHI: "IMPROVEMENT OF SINTERABILITY OF BA(MG1/3TA2/3)O3-POWDER COMPACTS BY BATA206 ADDITIONS" JOURNAL OF THE CERAMIC SOCIETY OF JAPAN, INTERNATIONAL EDITION, vol. 100, no. 12, 1 December 1992, pages 1441-1443, XP000303698	1-3, 7, 8, 11-13, 16-18, 21-23	
A		4-6, 9, 10, 14, 15, 19, 20, 24-30, 32	
	* abstract * * page 1441, left-hand column, paragraph 1 - page 1442, left-hand column, paragraph 3 *		
X	DATABASE WPI Section Ch, Week 9328 Derwent Publications Ltd., London, GB: Class L02, AN 93-224146 XP002052762 & JP 05 148 005 A (TAIYO YUDEN KK), 15 June 1993	1, 11, 21	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	* abstract *	4, 5, 7-10, 14, 15, 17-20, 22-29	
A	EP 0 399 770 A (NIPPON DENGYO KOSAKU KK :NGK SPARK PLUG CO) * column 1, line 7 - line 25 * * figure 1 *	11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 1998	Examiner Rosenberger, J
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 97 11 8539

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
T	LEE C C ET AL: "Effect of La/K A-site Substitutions on the Ordering of Ba(Zn _{1/3} Ta _{2/3})O ₃ " JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 80, no. 11, November 1997, pages 2885-2890, XP002053000 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 1998	Examiner Rosenberger, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)